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**Report written by:
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Final Report — Contract F49620-91-C-0065

Abstract

We have developed a novel technique for processing bulk high temperature superconductors and other ceramics under precisely controlled conditions of pressure, temperature, atmospheric composition, and strain rate. We achieve essentially uni-axial deformation of a pre-compacted disc inside a bellows-like capsule with massive end plates or "anvils". The capsule is located inside a Hot Isostatic Press (HIP), but has an independent gas supply. This makes it possible to maintain a specified gaseous atmosphere within the capsule and exert considerable forces on its contents *via* the anvils, simply by manipulating the two gas pressures. We call the process **Differential Pressure HIP Forging**, or DPHF, and are filing a patent application on the modifications to the, otherwise, conventional apparatus. DPHF opens a new regime for processing sensitive materials at elevated pressures and temperatures. The work was performed as part of a Phase 2 SBIR project, sponsored by SDIO (BMDO) and managed by AFOSR under contract F49620-91-C-0065.

Objectives

Our primary reason for developing a technique for forging ceramics in a controlled-atmosphere is to improve the critical current densities in discs and rings of bulk high temperature superconductors through densification and texturing. There are a number of applications for superconductors that do not depend on and should not have to wait for the availability of the conductor materials in wire or tape form. This includes superconducting bearings, superconducting "permanent" magnets and superconducting flux shields. As discussed in the final report on Phase 1 of the present effort (Laquer *et al.* 1992), our choice of material on which to check out these concepts has been the $Y_1Ba_2Cu_4O_8$ compound in the YBCO system. This particular composition, usually designated as 124, exhibits much greater thermodynamic stability than the more widely studied 123 composition. However, to remain stable at the temperatures of interest, 124 requires oxygen partial pressures in the 100 to 200 bar (1500 to 3000 psi) range.

Conventional Approaches

Densification of bulk ceramic powders is usually accomplished by sintering, or by uniform, tri-axial, isostatic hot pressing in a Hot Isostatic Press, or HIP, but with most high temperature, oxide superconductors these procedures have to be more elaborate. The chemical instability of these substances calls for careful selection of any contacting materials, as well as precise control of the oxygen partial pressure during all processing at elevated temperatures. At the same time, one must guard against any reaction between the oxygen and other oxidizable materials (including most metals) that are present within the container.

Texturing, on the other hand, is best achieved by uni-axial deformation, preferably at elevated temperatures, and is usually done by rolling, pressing, or forging. Unfortunately, the maintenance of an appropriate oxygen pressure is difficult and could indeed be quite hazardous with most equipment that can provide deformation in one direction, while not restraining the free flow of material in the other directions. Commercial equipment exists, where a compressive force is transmitted into a furnace by graphite rods, but the magnitude of the pressures that can be applied is generally less than 30 bar.

We thus have to implement four distinct requirements in order to attain our objectives:

- 1) Uni-axial hot deformation,
- 2) Control of the gaseous environment,
- 3) Minimization of hazards from hot oxygen gas at high pressures, and
- 4) Avoidance of contamination of the superconductor by contacting solids.

Alternative Concepts

The figures illustrate the development of our ideas on how to implement these four requirements. Fig. 1 sketches how a sealed bellows-like capsule with massive end pieces or "anvils" can be used inside a conventional HIP to provide uni-axial, rather than isostatic deformation of its contents.



Fig. 1 – Sealed Bellows Capsule

The sealed capsule of the indicated shape and proportions meets the first requirement, but does not readily allow maintenance and control of the gas composition and pressure inside the capsule. Neither is it possible to increase the rate of application of the compressive force beyond

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the limitations of the installed compressor system, typically of the order of 10s of minutes. The inclusion of a precisely measured quantity of an oxygen releasing compound, such as $KMnO_4$, within the capsule could help with modifying the gaseous atmosphere, but not necessarily at the desired time or temperature. Only a separate gas connection, as shown in Fig 2, permits fully independent control of the atmosphere within the capsule. This removes most restrictions on timing, temperature, pressurization, and pressure difference. Moreover, it facilitates applying large forces at widely adjustable rates to the contents of the capsule by simply venting some of its gas. We call this process **Differential Pressure HIP Forging**, or **DPHF**. It combines the inherent control of the gaseous environment in a hot isostatic press with the ability to apply large uni-directional forces and thus meets requirements (1) and (2).

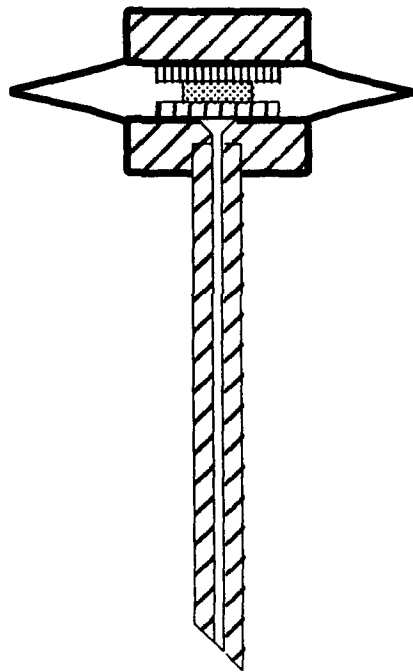


Fig. 2 – Differential Pressure Capsule

The third objective can be attained by limiting the reactive gas to the inside of the capsule and by an appropriate choice of construction materials, as well as by precautions and care in operating the system. For oxygen, the preferred capsule material is Monel 400, a commercial 20% copper - 80% nickel alloy. Its oxygen tolerance at elevated temperatures is only exceeded by the platinum alloys.

The fourth requirement, as also shown in Fig. 2 and discussed in more detail later, is met by placing ceramic discs between the superconductor pellet and the metal anvils. The disc near the gas inlet should be porous, or at least contain gas passages or channels to permit gas to contact the superconductor and allow flow in and out of the capsule, but the other disc could be solid or could even be replaced by a thin ceramic coating.

Modifications of the HIP

A 2000 bar (30,000 psi), *circa* 1980 Model SL-1 Mini-HIPper Laboratory Press, originally built by Conaway Pressure Systems Inc., was rebuilt with a Hoskins furnace to allow operation with a 20% Oxygen - 80% Argon gas mixture. It also had a high pressure gas feed-through installed in its bottom plate. A gas manifold and electronic pressure gauges were installed to measure the pressure in the capsule and to control the pressure difference between the capsule and the main HIP vessel to better than 0.05% (15 psi). The HIP was also fitted with a modern programmable temperature controller and connected to a digital data recording system.

Capsule Design

Fig. 3 shows the presently preferred implementation of the differential pressure pressing capsule. As already mentioned, the capsule is made entirely of Monel 400. It is supported by a stem of Monel high-pressure tubing with a fitting (not shown) that is screwed into the gas feed-through in the bottom plate of the HIP. The gas seal is made against the inside of the bottom plate by a captive silicone rubber O-ring. The seal design does not permit large excess pressures within the capsule (and neither does the capsule itself), but it does support capsule pressures that are less than the HIP pressure by 300 bar or more during the critical parts of the procedure.

The capsule is assembled by inert gas welding of its components. The relatively thin vertical extensions on the upper parts allow the final weld to be made without excessive heating of the contents. In principle, all functional requirements could be implemented with the simpler bellows design of Fig. 2. However, the more complex "top-hat" design presents a tradeoff between machining costs and complexity, on one hand, and ease and reliability of the final sealing assembly on the other.

Materials Interfaces and Diffusion Barriers

Although Monel does not react violently with the 20% O₂-80% Ar mixture at our maximum operating temperatures, it can reduce, *i.e.*, pull oxygen out of most oxide superconductors under these conditions. Silver has become the generally accepted and preferred interface or container material for most of these superconductors. Unfortunately, it also forms an oxide of variable, pressure-dependent composition, which in turn produces an unacceptably low melting eutectic with the remaining silver. A spray-on Ytria (Y₂O₃) ceramic (XYZ Coatings, Oak Ridge, TN) appears to be a suitable diffusion and reaction barrier on both Monel and alumina ceramics (see below).

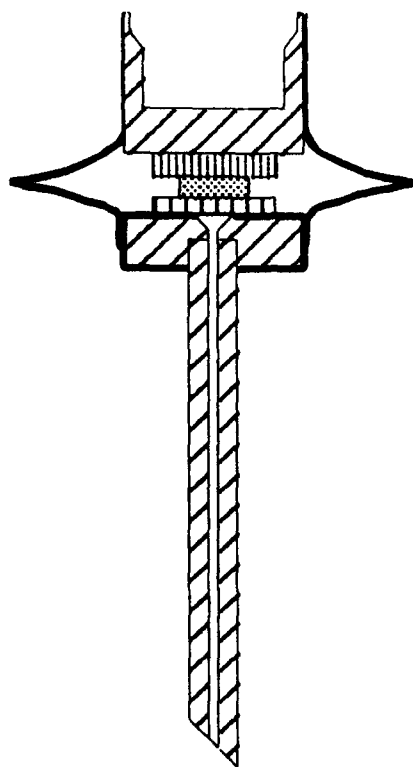


Fig. 3 – Capsule with Top Hat for Welding

Ceramic Anvils and Diffusers

For temperatures above 800C and under the necessary forces, Monel will undergo some plastic deformation and not remain perfectly flat, even at a thickness of 6 mm. For this reason, we interpose ceramic discs, or "pusher" plates between the heavy monel anvils and the superconductor. As mentioned, high purity alumina is suitable when coated with yttria.

There has to be free access from the high pressure tubing to the center of the capsule, in order to control the gas composition at the superconductor and the pressure within the capsule. This is best done by making the lower ceramic disc a porous one. Porous alumina is readily available and can have the surface in contact with the superconductor sprayed with yttria, without unduly restricting the gas flow. We have also used especially ordered porous yttria discs (Custom Specialty Ceramics, Arvada, CO), which provide even better chemical compatibility.

Operations

Pressure Control

To make the DPHF process work, we need proper operational procedures in addition to the novel equipment that has been developed. Ideally, the gas supply for the capsule should be totally independent from that of the main HIP. However, there are at least three reasons that would make coordinated manual control of the pressure in the two gas spaces quite difficult. First, the capsule volume is much smaller than that of the main vessel; second, the relative importance of the "dead" volumes at ambient temperature is different; and third, the capsule is at an essentially constant temperature, whereas the gas in the main vessel sustains a large temperature gradient. This means that in addition to installing a separate compressor, one would have to obtain rather complex and costly equipment to have the two systems accurately track during the pressurization and heating cycles.

An alternative to the independent control of the HIP and capsule pressures would be to insert a floating 1:1 piston of sufficient volume between the two systems. A still simpler, but less efficient, substitute for a the floating piston is to take advantage of the slowness of gas diffusion or mixing in a length of high pressure tubing. This, then, has been our compromise, together with making the furnace in the main HIP vessel of the oxygen-tolerant Hoskins type. Our apparatus simply uses an "equalizer" valve between the two systems. It also uses a "metering", needle valve in the gas supply to throttle the initial inrush of gas. This avoids excess pressure differentials, due to the differences in flow impedance, which can appear even when the equalizer valve is open.

The rest of the equipment differs little from that of a standard HIP. It consists of a gas manifold with pure Ar gas in commercial cylinders at a nominal 150 bar (2200 psi) and the 80% Ar-20% O₂ mixed gas supply at the same nominal pressure, piping and valving from the manifold to a 1700 bar (25,000 psi) air-operated gas compressor (Haskell), the hot isostatic press with its internal furnace, venting valves, a safety relief valve and exhaust piping. There are also a number of interlocks, check valves and other safety devices, pressure gauges, thermocouple thermometers, and a temperature programmer/controller for the 15 kW furnace power supply.

To recapitulate, the only non-standard equipment associated with operating the capsule inside the furnace, is the needle valve to slow down the initial inrush, the equalizer valve, to reduce costly duplication of compressors, long tubing to mimic a 1:1 piston, a separate vent valve and matched pressure gauges to allow differential measurements of sufficient precision.

Pressurization

The usual operating procedure for a HIP is to compress the gas near room temperature to a pre-established pressure and then heat the system to its operating temperature, while the pressure automatically rises to the desired value. It should be noted that the final pressure is less than one would calculate from a simple application of the gas laws, because of the previously mentioned temperature gradient between the water-cooled walls and the furnace.

Our procedure is to bring the entire apparatus to about 300 bar with the Ar-O₂ mixture and then to raise the pressure to about 600 bar with pure argon, before starting the furnace. We also keep the equalizer between the HIP and the capsule open during the entire pressurization, except for a leak check just before starting the heating cycle. This constraint is partly due to the previously mentioned limitations of the mechanical design, but mainly due to our desire to completely control the forging temperature, pressure and time. As mentioned, the precision metering valve in the line from the gas manifold, in parallel with the regular full-flow valve, is used to slow down the initial filling of the system to the supply pressure, prior to starting the compressor.

The pressurization by the air-operated compressor is the most time consuming part of our procedure. The actual limitation is not set by the capacity of the Haskell high-pressure compressor, but rather by that of the small 5 hp air compressor that furnishes the driving power. Replacement by an electric motor powered gas compressor could greatly speed the process.

Heating Cycle

We can easily ramp the furnace at rates from 2 to 20 C/min, but usually slow down to 5 C/min for the last 50 C, prior to reaching the holding temperature. With this procedure, the temperature never overshoots the set-point by more than 1 or 2 C.

Forging

Before starting the forging operation, we repeat the leak check by closing the equalizer and watch the pressure difference between the capsule and the HIP vessel. This verifies that all of the high pressure valves are completely closed. Then by either gradually or more quickly opening the capsule exhaust valve, we can control the pressure difference and thereby forge the contents of the capsule at a wide range of strain rates. To date, we have been able to apply pressures as large as 300 bar in as little as 3 seconds, or as long as 20 minutes.

Cool-Down

The temperature controller can also program the cool-down of the furnace, but in most situations it appears best to actually "quench" the material by simply shutting off the furnace. We have observed initial quench rates as high as 50C/min and it should be possible to increase this by simultaneously venting the HIP to obtain additional cooling from the adiabatic expansion of the high pressure gas. The only restriction is not to allow the pressure in the capsule to become larger than the pressure in the main vessel.

Gas Analysis

It is essential that we should know the actual oxygen concentration in the gas that is in contact with the superconductor with reasonable accuracy, since this is the most important parameter in defining the process. An electrochemical oxygen analyzer (Rosemount Analytical, Mod 715) on the exhaust gas stream allows us to read oxygen concentrations in argon on the 25% full scale range of the instrument with a resolution of better than 0.25%, or 1% of full scale.

Results

Hot Pressing

Our primary effort under AFOSR contract F49620-91-C-0065 has been the development of the technique and equipment for deforming high temperature ceramic superconductors, under carefully controlled conditions of temperature, pressure and gaseous environment. Fig. 4 shows temperature and pressure profiles for the compression and initial cool-down parts of a typical run. The light lines near the top of the graph are the pressures in the HIP vessel and in the capsule. The heavy line near the bottom is the pressure difference, which generates the compressive force on the sample. The heavy line near the top indicates the millivoltage from the Type R thermocouple next to the capsule. In this particular run we changed from "scramming" the furnace to programmed cool-down, as seen after the sharp dip.

HIP Run 19

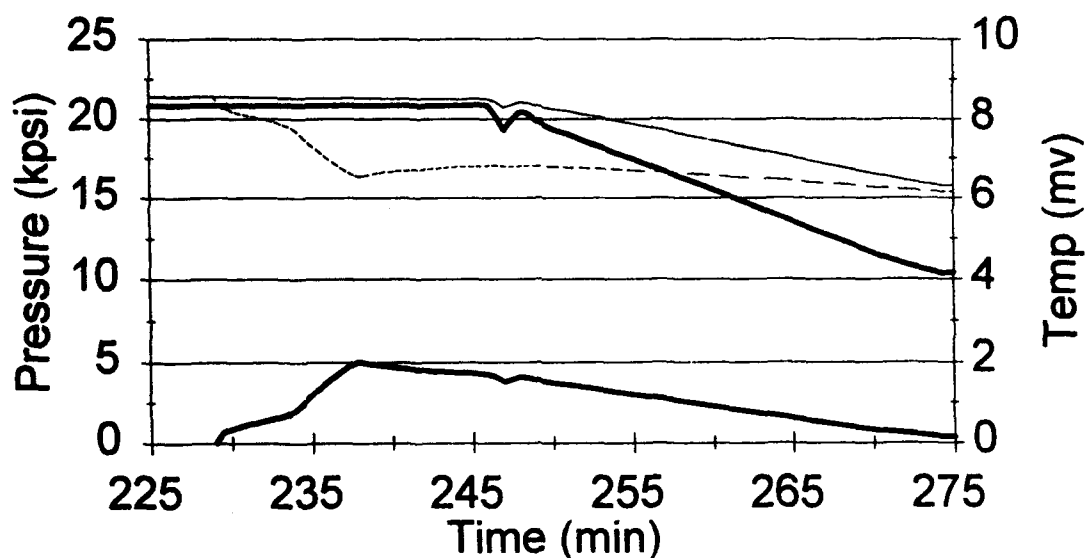


Fig. 4 —Compression and Cool-Down of Capsule

Fig. 5 shows a group of fully and partially assembled capsules prior to being hot pressed and Fig. 6 shows a processed capsule. We can measure the axial compression of the contents by measuring the height of the assembly before and after a run.

Fig. 7 shows a capsule cut open with the top and bottom halves separated and Fig. 8 shows the resulting compacted disc of superconductor. This particular sample increased in diameter from 19 to 24 mm, while decreasing in thickness from 3 to 1.5 mm.

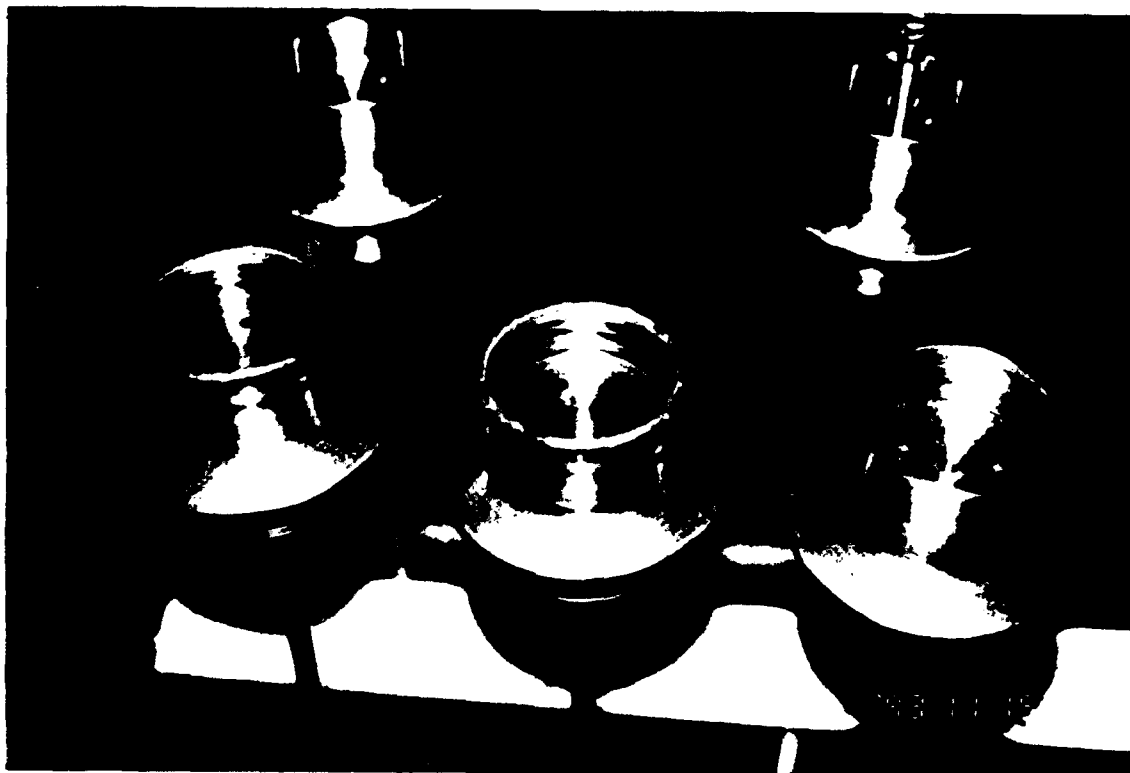


Fig. 5 — Fully and Partly Assembled Capsules



Fig. 6 — Processed Capsule

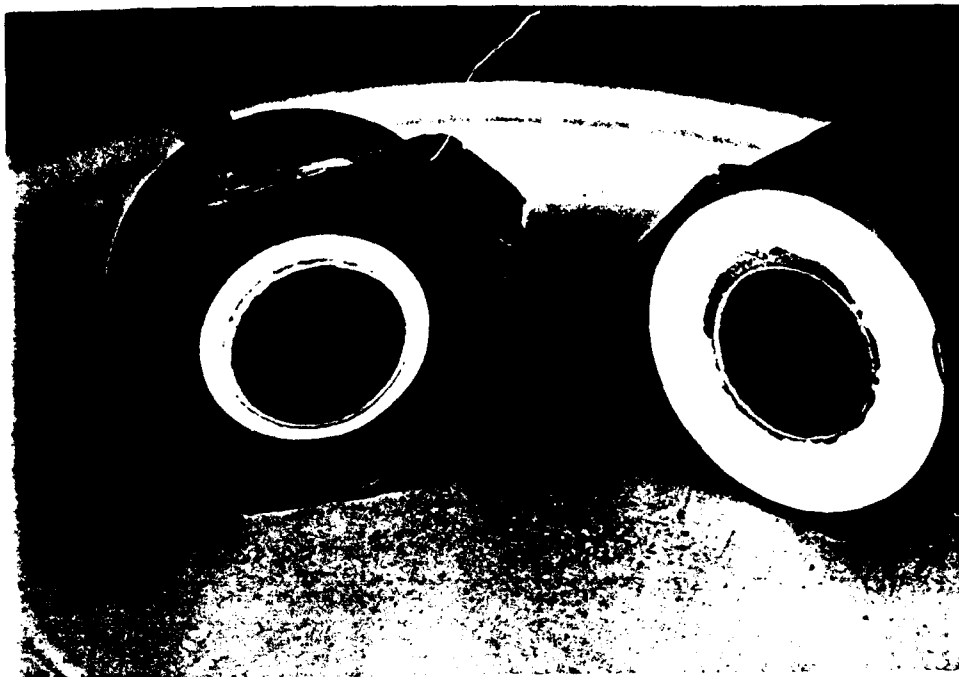


Fig. 7 — Split Capsule after Processing



Fig. 8 — Hot Pressed Superconducting Disc - 24mm diameter

Parallel Efforts

In spite of the tremendous effort worldwide on the high temperature superconductors, there is a surprising dearth of a equipment or facilities to measure the properties of real bulk samples in the 20 to 70K temperature interval. Most apparatus is either limited to specimens of less than 3 mm diameter, or to the narrow temperature ranges of various cryogenic liquids (and then often only at their boiling points).

We have, therefore, assembled a cryogenic refrigerator that allows us to reach temperatures as low as 13K and we have installed electronic equipment to measure the AC susceptibility of the bulk discs of 10 to 25 mm diameter, that are produced in the hot forging operation. Fig. 9 plots, as a function of temperature, the voltage induced in a pickup coil by a driver coil on the opposite side of a 12 mm disc of 124-YBCO. The figure also gives the slope of that signal (dashed line). It suggests a superconducting transition, starting near the expected temperature of 82K, but there is some uncertainty, since we used an old single phase lock-in amplifier, which could not completely separate the susceptibility signal from direct pickup.

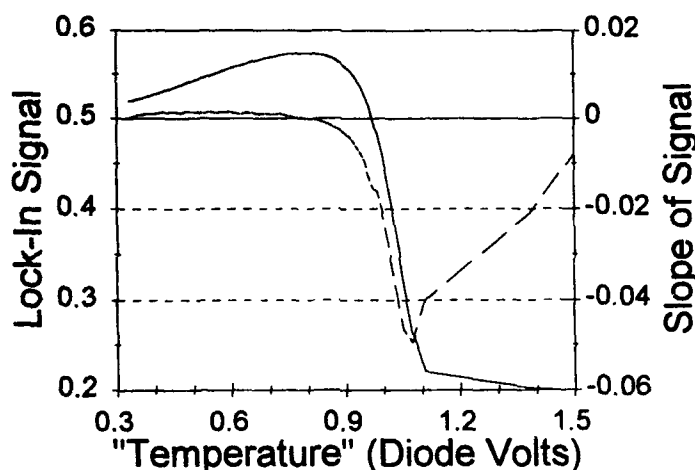


Fig. 9 — Superconducting Transition in Hot Pressed Disc

We have since acquired (with company funds) a modern, digital, dual phase lock-in amplifier, as well of state-of-the-art data acquisition equipment and are in the process of integrating these instruments. We had hoped to include some new results in this report, but have, been unable to do so before its due-date. The work is continuing under company sponsorship.

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